Supplementary Information: First-principles investigation on anion order, electronic structure and dielectric properties of $BaTaO_2N$

Xi Xu and Hong Jiang*

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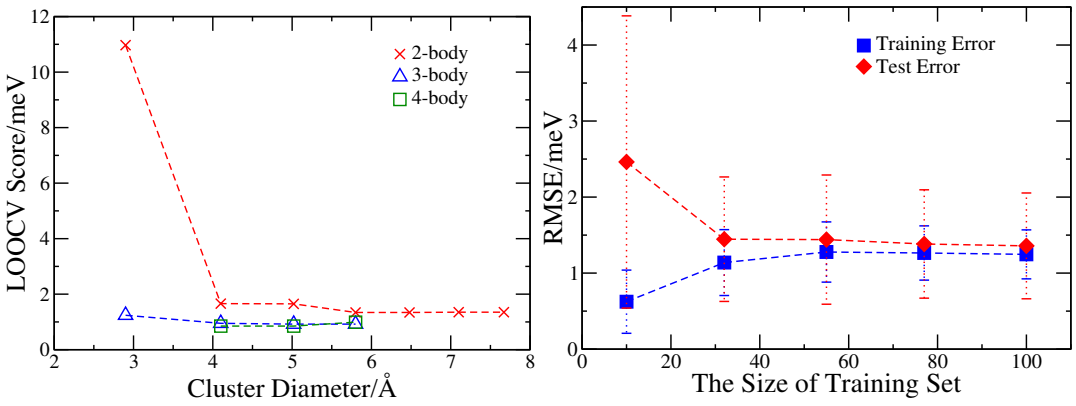
Table S1: Cluster functions of 40-atom SQoS and SQS, compared with the target cluster correlation functions (CCFs) of the $15 \times 15 \times 15$ supercell at $T = 1300$ K and cluster correlation functions for the totally random state respectively.

Index of two-body clusters	SQoS	CCF(1300 K)	SQS	CCF($T = \infty$)
1	0.042	0.050	0.083	0.111
2	-0.167	-0.225	0.167	0.111
3	0.083	0.081	0.000	0.111
4	0.104	0.115	0.104	0.111
5	0.125	0.125	0.083	0.111
6	0.083	0.099	0.083	0.111



(a) (b)

Figure S1: (a) The leave-one-out cross validation (LOOCV) scores with respect to different cluster expansion models. Candidates of cluster expansion models are generated by the following hierarchical approach: null and point clusters are always included. Two-body clusters are added step by step in terms of their diameters until the LOOCV score does not decrease significantly any more. Once two-body clusters are selected, three- and four-body clusters are added to the CE model in turn following the same procedure. Since the addition of three- and four-body clusters makes little difference, we adopt the cluster expansion model with one null cluster, one point cluster and six two-body clusters as our working model. (b) Learning curves for our working model with least-squares fitting of ECIs. Errors are in the unit of meV per atom. Training sets and test sets are generated by repeated 5-fold cross validation with the help of Scikit-learn code.[1]

Table S2: Zone-center ($\mathbf{q} = 0$) optic phonon frequencies (unit: cm^{-1}) for the three representative structures (MSC, SQoS and SQS).

	MSC	SQoS	SQS
1	79.06	48.34	71.26
2	81.58	61.62	76.94
3	85.57	67.88	82.98
4	86.59	76.15	83.97
5	87.51	81.29	90.51
6	89.10	87.62	93.82
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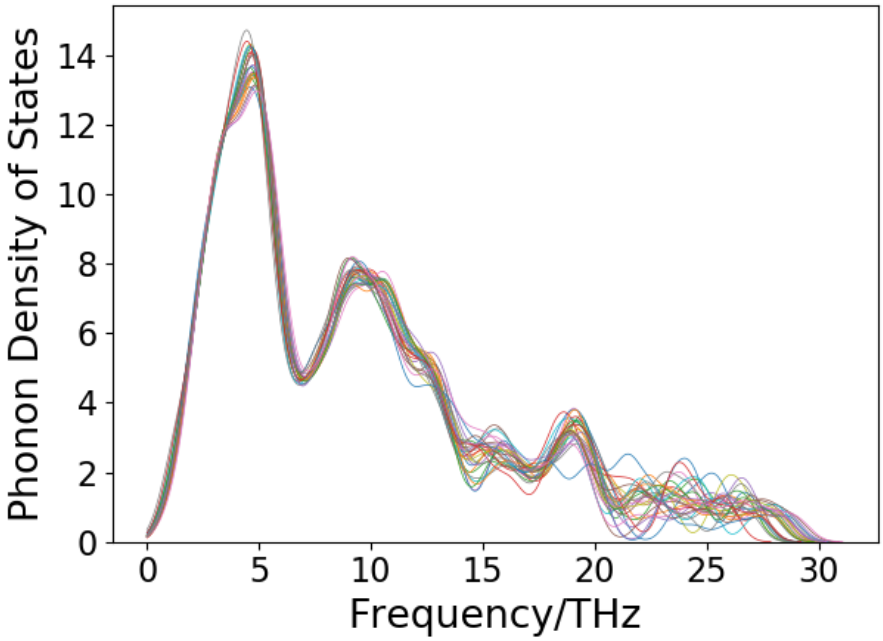


Figure S2: The phonon density of states for the 28 structures used in the cluster expansion of the free energy. No imaginary frequency is found for any structures.

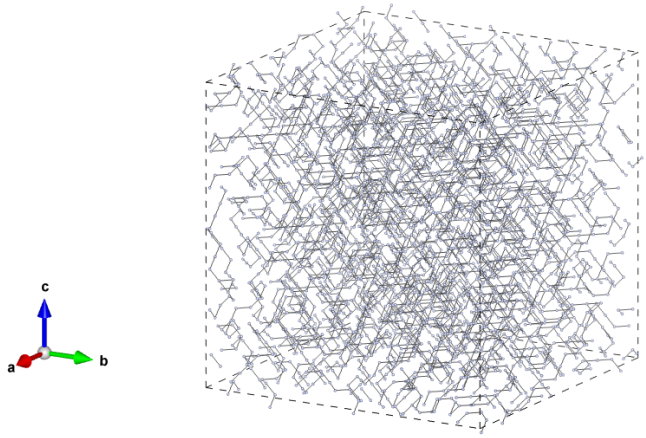


Figure S3: A snapshot from Monte Carlo simulations of the $15 \times 15 \times 15$ supercell of $BaTaO_2N$ at $T = 300$ K. N atoms are represented by small blue balls and O atoms are omitted for clarity. Two N atoms in the adjacent positions are connected by a grey bond. It can be seen that N atoms are distributed almost uniformly and most octahedra take the *cis* configuration.

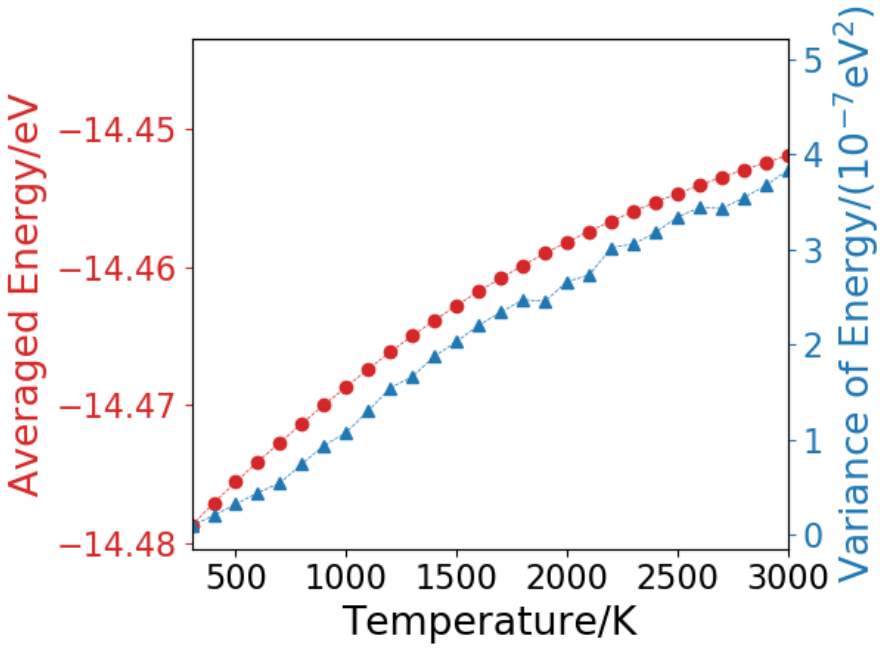
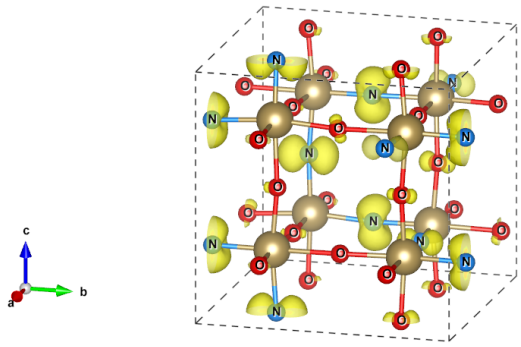
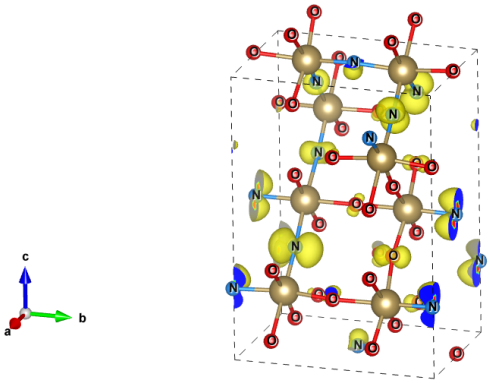


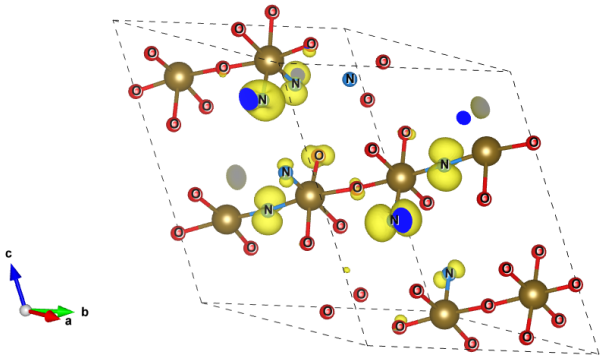
Figure S4: The ensemble averaged energy and its variance from Monte Carlo simulations of the $15 \times 15 \times 15$ supercell of $BaTaO_2N$ at different temperatures. Both increase "continuously" as the temperature rises, indicating that there is no sign for first-order or second order phase change at the range of considered temperatures.



(a) MSC



(b) SQoS



(c) SQS

Figure S5: Decomposed charge density at the valance band maximum of MSC, SQoS and SQS. Ta atoms are shown by large brown balls. O and N atoms are represented by red and blue small balls respectively. Ba atoms are omitted for their negligible contributions.

References

[1] F. Pedregosa, G. Varoquaux, A. Gramfort, V. Michel, B. Thirion, O. Grisel, M. Blondel, P. Prettenhofer, R. Weiss, V. Dubourg, J. Vanderplas, A. Passos, D. Cournapeau, M. Brucher, M. Perrot and E. Duchesnay *J. Mach. Learn. Res.*, **2011**, 12, 2825–2830.